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6055198002

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation **United Kingdom**

4. Title of the invention **Catalyst**

5. Name of your agent (if you have one) **BOULT WADE TENNANT**

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Abstract

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CATALYST

The present invention relates to a process for preparing a supported catalyst or catalyst precursor, to a process for carrying out a chemical reaction utilizing such a catalyst, and to a Fischer-Tropsch synthesis catalyst.

Catalysts are well known to be useful in certain reactions. In particular, they can be used to promote particular reactions that would not normally take place in the absence of the catalyst.

A typical catalyst comprises one or more catalytically active components supported on a catalyst support. Typically, the catalytically active components are metals and/or metal-containing compounds. The support materials are generally high surface area materials with specific pore volumes and distribution.

Various methods for depositing catalytically active components on catalyst supports are known. For example, the catalyst support may be impregnated with an aqueous solution of the catalytically active component(s). The impregnated support may then be dried, and calcined. An example of such an impregnation technique is described in WO 01/96017.

The catalytically active component may also be deposited onto the catalyst support by precipitation. In EP 0569624, for example, a catalyst support is first impregnated in an aqueous solution of a noble metal. The metal is then precipitated onto the support by contacting the impregnated support with an aqueous solution of an alkali metal salt.

A further method of depositing a catalytically active component on a catalyst support is the sol-gel method. In the sol-gel method, a metal oxide is hydrolysed in the presence of a stabiliser, such as an amphiphilic betaine, to produce colloidal particles of the metal oxide. The particles may be co-precipitated onto a support formed of gel precursors of, for example, hydrolysed $\text{Si}(\text{OMe})_4$. An example of such a process is described in DE 19852547.

10

A new process for process for producing a catalyst has now been developed. In particular, the process of the present invention enables a catalytically active component(s) or its precursor(s) to be deposited on a support in a controlled manner. Accordingly, certain properties of the catalyst, for example its activity and/or selectivity, may be controlled.

15

According to a first aspect of the present invention, there is provided a process for preparing a supported catalyst or catalyst precursor comprising:

20

a. preparing a liquid mixture of (i) a catalyst support or a catalyst support precursor; (ii) a metal-containing compound and (iii) a polar organic compound which acts as a solvent for the metal-containing compound;

25

b. converting said mixture to a paste or solid residue; and

c. combusting the residue in an oxygen-containing atmosphere to at least partially convert the organic compound to carbon and to form said supported catalyst or catalyst precursor.

30

According to a second aspect of the present invention, there is provided a process for preparing a supported catalyst or catalyst precursor comprising:

- a. preparing a mixture of (i) a porous catalyst support and (ii) an organic compound in a solvent;
- b. removing the solvent such that the polar organic compound is deposited in the pores of the catalyst support;
- c. mixing the catalyst support with a solution of a metal-containing compound and removing the solvent to form a solid residue or kneading or mechanical mixing the catalyst support with a metal-containing compound; and
- d. combusting the resultant solid in an oxygen-containing atmosphere to at least partially convert the organic compound to carbon and to form said supported catalyst or catalyst precursor.

The present invention also provides a process for carrying out a Fischer-Tropsch synthesis, hydrotreating or hydrocarbon partial oxidation reaction, which comprises catalysing said reaction with a catalyst prepared by a process as defined above.

The present invention additionally provides a Fischer-Tropsch synthesis catalyst or catalyst precursor comprising, on an inert support,

- i) 10 to 40 wt% cobalt, nickel or a mixture thereof;
- ii) 1 to 10wt% promoter selected from zirconium, uranium, titanium, thorium, hafnium, cerium, lanthanum, yttrium, magnesium, calcium, strontium, cesium, rubidium, molybdenum, tungsten, chromium, manganese, rhenium and rare earth elements; and
- iii) carbon in an amount of up to 8 wt%;

the above percentages being based on the total weight of the supported catalyst. The catalyst or catalyst precursor may be non-activated or activated, for example by hydrogen or hydrocarbon gas or vapour.

5

Catalysts and catalyst precursors produced by the processes of the present invention may be employed in a number of reactions. For example, the catalysts and catalyst precursors produced by the processes of the present
10 invention may be used in Fischer-Tropsch synthesis, or to catalyse the partial oxidation of a hydrocarbon, such as methane (POM).

As used herein, the term "catalyst" covers the catalyst in
15 active form. The term "catalyst precursor" covers the catalyst in precursor form, since it may undergo change in the reaction environment.

The first aspect of the invention will now be further
20 described.

In step a), a liquid mixture is prepared from at least three components: (i) a catalyst support or a catalyst support precursor; (ii) one or more metal-containing compound(s) and
25 (iii) one or more polar organic compound solvents which act as solvent(s) for the metal-containing compound(s).

All three components may be mixed together simultaneously. The components may be mixed together at room or elevated
30 temperature, for example, at 20 to 200°C, preferably 40 to 80°C, more preferably 40 to 60°C.

In an alternative embodiment, two of the three components may be mixed together in a preliminary step, before the third component is added to complete the liquid mixture. Preferably, components (ii) and (iii) are mixed together in a preliminary step. These two components may form a clear solution. Thereafter, component (i) may be added to complete the liquid mixture - which will contain solid particles if component (i) is a solid support. The liquid mixture may be formed at elevated temperature, for example, at 20 to 200°C, preferably 30 to 80°C.

As mentioned above, component (i) is a catalyst support or catalyst support precursor. A catalyst support is generally in the form of one or more solid particles. In contrast, the catalyst support precursor may initially be in liquid form or in the form of a solution. The support precursor may form a solid catalyst support *in situ*, for example, once the catalyst support precursor has been added to the liquid mixture. In a preferred embodiment, the catalyst support precursor forms a catalyst support in the conversion or combustion step (steps b or c).

Suitable catalyst supports include inert supports or active supports.

25

Examples of suitable supports include solid oxides, carbides, zeolites, carbon and boronitride, especially alumina, modified alumina, spinel oxides, silica, modified silica, magnesia, titania, zirconia, a molecular sieve, a zeolite, β -aluminate and forms of carbon. The alumina or modified alumina may be, for example, α -alumina, β -alumina or γ -alumina. β -alumina and spinel oxides such as barium

hexaaluminate have been found to be particularly useful in view of their stability. The carbon may be in the form, for example, of active carbon or carbon nanotubes. A zeolite may be chosen depending on the desired final product. Thus, 5 for example, it may comprise pores or channels. Suitable zeolites are zeolites A, X, Y, ZSMs, MCMs or AlPO_4 .

Suitable catalyst support precursors may be derived from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{Mg}(\text{NO}_3)_2$. Suitable catalyst precursors are 10 described in further detail in Gonzales et al, Catalysis Today, 35 (1997), 293 - 317 and J. Livage, Catalysis Today, 41 (1998), 3 - 19.

In one embodiment of the invention, the catalyst support is 15 derived from a nitrate of, for example, a Group IIA or Group IIIA metal. For example, aluminium or magnesium nitrate may be used. Preferably, the nitrate is in hydrated form. Examples of such nitrates are $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In step a, this nitrate may be mixed with an organic 20 compound, such as urea and/or ammonium citrate, to form a clear solution. Water may optionally be added. To complete the liquid mixture, a metal-containing compound, such as cobalt nitrate, is included in the mixture. During one of the subsequent conversion and combustion steps (steps b and 25 c), a supported catalyst or supported catalyst precursor is formed.

The catalyst support employed in the first aspect of the invention is preferably porous. The particle size is 30 desirably $0.1\mu\text{m}$ to 20mm , preferably, $0.2\mu\text{m}$ to 5mm , depending on the application. The surface area is desirably greater than $100\text{m}^2/\text{g}$ measured at 25°C and 1atm .

preferably greater than 50 m²/g, for example, greater than 200 m²/g. One or a mixture of two or more catalyst supports may be used.

5 Component (ii) of the liquid mixture is a metal-containing compound. One or more metal containing compounds may be used. Generally, the catalytically active component of the catalyst is, or is derived from, this metal-containing compound. Suitable metal-containing compounds are well known
10 in the art. For example, the metal-containing compound comprises at least one metal selected from the lanthanide, actinide and transition metal series of the Periodic Table. Preferably, the metal-containing compound comprises an f-block or d-block metal.

15

Preferred metals are one or more selected from noble metals such as Pd, Pt, Rh, Ru, Ir, Au, Ag and Os, and transition metal elements such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Nb, Mo, Tc, Cd, Hf, Ta, W, Re, Hg, Tl and the 4f-block
20 lanthanides such as La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Of these metals, Pd, Pt, Ru, Ni, Co, Fe, Cu, Mn, Mo and W are preferred.

The metal-containing compound may contain other elements,
25 although one skilled in the art will recognise that an appropriate choice may have to be made depending on the final use of the catalyst and the preparation conditions. Preferably the metal-containing compound is in the form of a salt. Examples of suitable metal-containing salts are
30 nitrates, citrates, halides, alkoxides, phenoxides, acetates, benzoates, oxalates and acetylacetonates

Component (iii) of the liquid mixture is a polar organic compound. The organic compound functions as a solvent for component (ii) and may act as a solvent for compound (i). The organic compound may be any polar organic compound that is capable of undergoing combustion in the presence of an oxygen-containing atmosphere such as air. A distinguishing feature of combustion is that a flame can often be seen during the combustion. It is a necessary feature of the combustion that the organic compound is converted to carbon which may be present either as elemental carbon or as a carbide, for example a carbide of the metal of the metal-containing compound (ii). Some or all of the organic compound may be converted to carbon, and it is also possible for some of the organic compound to be completely combusted such that the carbon is converted to carbon monoxide or carbon dioxide and is removed from the catalyst or catalyst precursor as a gas. Preferably, the organic compound is one that does not produce an ash, in particular an oxide ash, after the combustion step. Preferably, therefore, the organic compound is one that does not contain elements that have a tendency to form involatile residues such as oxides after combustion. Such elements include, for example, metals, phosphorus and/or silicon.

Examples of suitable organic compounds are organic amines, organic carboxylic acids and salts thereof such as ammonium salts, alcohols, ammonium salts of phenoxides and alkoxides, amino acids and surfactants. Preferred alcohols are those containing from 1 to 30 carbon atoms, preferably, 1 to 15 carbon atoms. Examples of suitable alcohols include methanol, ethanol and glycol. A preferred carboxylic acid is acetic acid.

compounds are compounds containing functional groups such as one or more hydroxyl, amine, amide, carboxylic acid, ester, aldehyde, ketone, imine or imide groups. Suitable compounds include urea, hydroamines, trimethylamine, triethylamine, 5. tetra methylamine chloride and tetraethylamine chloride. Preferred organic compounds include EDTA, urea and/or ammonium citrate

The organic compound may be in the form of a liquid at room 10 temperature (20°C) or at the temperature at which the mixture is prepared. The organic compound may be heated before it is added to the mixture. The organic compound may also be in the form of a solid at room temperature or at the temperature at which the mixture is prepared, in which case 15 the mixture is heated after it is prepared to melt the organic compound. Mixtures of organic compounds can be used. Water may also be added, particularly, when the organic compound does not melt even upon heating.

20 When water is employed in the liquid mixture, the amount of water may need to be controlled. For example, certain catalyst support precursors, such as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ have a tendency to form polymeric gels on coming into contact with effective amounts of water. Thus, 25 the amount of water employed in step (a) is preferably kept to a minimum, to avoid the formation of a hydrolysed gel. Thus, the amount of water may be sufficient to partially hydrolyse the catalyst precursor, but not sufficient to convert the catalyst precursor into a polymer. Typically up 30 to 20 wt% water can be used with respect to the total weight of the mixture. However, some catalyst precursors, such as those based on cobalt and/or molybdenum, may require more

water, for example, up to 50 wt%. In other embodiments of the invention, the use of water is avoided altogether.

Water may be added separately or may, for example, be present in one of the components added as water of crystallisation or water of coordination.

The mixture may also comprise other components if desired. Other components that may be added to the liquid mixture include promoters and/or modifiers. Suitable promoters are alkaline earth salts such as magnesium, calcium, barium and/or strontium nitrate. Suitable modifiers are rare earth modifiers such as rare earth salts, for example lanthanum and/or cerium nitrate or acetate, or oxides of the d-block transition metals. Examples are oxides of phosphorus, boron, gallium, germanium, arsenic and antimony. The promoters and modifiers may be used singly or in a combination of two or more.

It is important that the mixture prepared in step (a) is a liquid mixture. By "liquid mixture", we mean that the mixture is in the form of a homogeneous liquid, although it may comprise solid particles. For instance, if a catalyst support rather than a catalyst support precursor is present, the liquid will usually comprise solid support particles. It is an essential aspect of the present invention that the metal-containing compound is able to contact the support or support precursor, and this is achieved by the use of a liquid mixture.

The weight ratio of component (i) : (ii) : (iii) employed in

60:2-80:10-90. It should be understood that the weight ratios may be varied depending on the intended use of the final catalyst. The amount of organic compound is generally determined by the atomic ratio of carbon in the organic
5 compound to metal (C:M) in the dissolved metal containing compound. Normally the atomic ratio is at least 0.4:1, preferably 1 to 20:1.

After the liquid mixture is formed, it is converted to a
10 paste or solid residue in step b. Desirably, this is achieved by heating the mixture. This heating step is in addition to any heating required to melt the organic compound, although if previous heating is required that heating can simply be continued in step b. The heating
15 transforms the liquid mixture into a solid, for example by evaporating or decomposing the organic solvent. Any water that may be present in the liquid mixture is also preferably evaporated. The temperature to which the mixture is heated may be any temperature above room temperature (20°C), for
20 example from 50°C to 250°C, and can be carried out for any time until a solid residue is formed, for example for from 1 to 24 hours. A combination of drying steps may be used. Thus, for example, the mixture may initially be dried at room temperature for from 2 to 10 hours, and subsequently
25 dried at an elevated temperature, for example from 100°C to 200°C, especially about 120°C.

In step c the mixture is combusted. Preferably, the combustion step is carried out in air. Alternatively, pure
30 oxygen or oxygen in an inert atmosphere of, for example, nitrogen or another inert gas may be employed. This combustion step may be separate from the heating in step b,

or the two steps may be combined, for example by simply continuing to heat the mixture after the solvent has been removed.

- 5 A suitable combustion temperature is, for example, from 200°C to 1000°C, especially from 400°C to 600°C. The combustion step may be performed for any time, but especially for a limited duration such as 30 minutes or less, preferably 15 minutes or less, especially for from 5 to 15 minutes. As
10 indicated above, the combustion step converts the polar organic compound into carbon and volatiles. It is also postulated, although we are not bound by this theory, that the combustion step changes the metal-containing compound into a metal and/or one or more oxide, oxycarbide or carbide
15 forms or mixtures thereof. The combustion step may also convert the promoter and/or modifier to oxide forms if they are present.

The catalyst preparation may, for example, proceed by first
20 mixing the metal containing compound(s) and polar organic compound(s). This mixture is usually viscous and addition to a solid catalyst support will mainly coat the external surface of the support, with only a limited penetration of "internal" surfaces such as pores. After the combustion
25 step, a so-called "egg-shell" catalyst in which all or substantially all of the catalyst is present on the surface of the support is obtained. Such a catalyst is useful for many reactions, in particular a Fischer-Tropsch synthesis reaction. We have surprisingly found that the process of
30 the present invention provides a better and more even distribution of the catalyst on the surface of the support than can be obtained by other methods.

The cobalt preparation may also, for example, proceed by first mixing the metal containing compound(s) with the organic compound(s) and a soluble support precursor then added. After combustion, the metal catalyst will be distributed on both the "external" and "internal" surfaces of the support. This catalyst can be used advantageously for partial oxidation of natural gas to synthesis gas and partial oxidation of gasoline into hydrogen. A more homogeneous distribution of the catalyst throughout the support may be obtained than in known catalysts.

The supported catalyst or catalyst precursor generally comprises from 0.5 to 50 wt% catalyst or catalyst precursor, 0 to 10 wt% promoter and 0 to 5 wt% modifier, based on the total weight of the supported catalyst or catalyst precursor. For a POM reaction the supported catalyst or catalyst precursor preferably comprises from 0.5 to 10 wt% catalyst or catalyst precursor, 0 to 5 wt% promoter and 0 to 3 wt% modifier. For a Fischer-Tropsch reaction the supported catalyst or catalyst precursor preferably comprises from 5 to 40 wt% catalyst or catalyst precursor, 0 to 3 wt% promoter and 0 to 3 wt% modifier. The above percentages for the catalyst or catalyst precursor are based either on the compound or the metal in the compound.

The supported catalyst precursor may, if desired, be activated, for example with hydrogen or hydrocarbon gas or vapour.

The second aspect of the invention will now be further described.

This aspect of the invention differs from the first aspect in that the initial mixture only necessarily comprises a porous catalyst support and a polar organic compound in a solvent. The metal-containing compound is not necessarily
5 present. In this aspect of the invention the solvent is removed, for example by heating, such that the organic compound is deposited in the pores of the catalyst support. The catalyst support is then mixed with the metal-containing compound, especially in the form of a solution wherein the
10 solvent is subsequently removed to form a solid residue. Alternatively, the catalyst support is kneaded with metal-containing compound. This process produces a supported catalyst or catalyst precursor in which the catalyst or
15 catalyst precursor is predominantly situated on the external surfaces of the porous particles. Such a catalyst is particularly useful as a catalyst for Fischer-Tropsch synthesis.

For the most part, the discussion concerning the first
20 aspect of the invention is also appropriate for the second aspect, in particular in regard to the porous catalyst support and metal-containing compound. Accordingly the discussion regarding the first aspect also applies to the second aspect and is herein incorporated by reference. In
25 step a of the second aspect of the present invention, however, the solvent in which the organic compound is dissolved may not only be a polar organic solvent, for example, one of those listed in respect of the first aspect of the present invention, but may also be a non-polar
30 organic solvent or water. The organic compound should, however, be solid at room temperature (20°C) so that it

effectively blocks the pores of the catalyst support when the solvent is removed.

As mentioned above, a solution of the metal-containing compound is employed in step c of the second aspect of the present invention. The metal-containing compound may be dissolved in any solvent, for example, a polar organic solvent such as those mentioned with respect to the first aspect of the present invention, a non-polar organic solvent or water. The solvent can again be removed by any means, for example by heating. If the catalyst support is kneaded with a metal-containing compound, the metal-containing compound is preferably solid at room temperature. The kneading may be carried out for a suitable time such that the surfaces of the support is coated with the metal-containing compound, for example for 1 hour or greater.

The process of the present invention provides a catalyst or catalyst precursor supported on the support. Depending on the nature of the reaction to be catalysed, the catalyst precursor may be distributed in any desired way on the "external" surface or in the "internal" surfaces of the support. Thus it may, for example, be distributed substantially throughout the support or only on the external surface of the support. By appropriate choice of starting materials and process conditions, it has been found that the distribution of the active catalyst component or precursor thereof can be carefully controlled.

The catalyst or catalyst precursor contains carbon, either as elemental carbon or in the form of a metal carbide or oxycarbide. The carbon content is especially up to 8 wt%

based on the total weight of the catalyst precursor or catalyst but is preferably from 0.01 to 2 wt% for better performance.

- 5 The catalyst or catalyst precursor produced by the process of the present invention may be used in any process where a catalyst may be used, especially when a fixed bed reactor is used. Thus, for example, it may be used in a POM reaction, Fischer-Tropsch reaction, or a hydrotreating reaction, for
10 example a hydroisomerisation reaction or a hydrogenation reaction.

In a POM reaction, a mixture of a hydrocarbon and oxygen is passed over the catalyst to produce syngas. The hydrocarbon
15 preferably contains from 1 to 16 carbon atoms and more preferably from 1 to 5 carbon atoms. Most preferably it is methane or natural gas. The hydrocarbon may be saturated or unsaturated, for example containing from 1, 2, 3 or more double and/or triple bonds. It may be linear, cyclic or
20 branched. The hydrocarbon may also be aliphatic and aryl or contain both aliphatic and aryl groups. One or a mixture of hydrocarbons may be used.

In the POM reaction the oxidant is normally O_2 . However, it
25 may be supplemented with H_2O (steam) or CO_2 , for example by addition to the feedstock. Thus O_2 and H_2O ; O_2 and CO_2 ; or O_2 , H_2O and CO_2 may be used. This results in oxy-steam or oxy-dry reforming of methane, respectively. By this means the exothermicity and product ratio may be controlled as
30 desired. The O_2 , and optionally H_2O and CO_2 may be used pure or diluted with an inert gas such as air, N_2 , Ar or He.

Desirably the reaction takes place at a temperature of at least 500°C, for example from 700°C to 1000°C. Desirably the pressure is atmospheric pressure (101 kPa) or above, for example from 1 to 30 atmospheres (101 kPa to 3040 kPa). The mole ratio of the hydrocarbon being oxidized and the oxygen is desirably chosen such that a mixture of carbon monoxide and hydrogen is obtained in a stoichiometric ratio. Thus, for example, the atomic ratio of carbon in the hydrocarbon such as methane to oxygen is desirably 1.8 to 3.5:1, especially about 2:1, although lower or higher ratios may also, if desired, be used.

The catalyst produced by the process of the present invention may also be used, for example, in a Fischer Tropsch synthesis reaction. Such a reaction produces a mixture of hydrocarbons and/or oxygenated hydrocarbons, for example gaseous, liquid and/or solid hydrocarbons and/or oxygenated hydrocarbons such as alcohols, from a mixture of hydrogen and carbon monoxide. Thus, for example, the reaction can be carried out immediately using syngas prepared by the POM method in directly linked reactors as disclosed in, for example, WO 01/36,323.

The present invention is now further illustrated in the following Examples.

EXAMPLES

Example 1

5 Preparation of a cobalt Fischer-Tropsch synthesis catalyst

Co(NO₃)₂.6H₂O (16g) was mixed with UO(NO₃)₂.2H₂O(1.3g), then urea (14.2g) was added in a mole ratio of urea to metal of 4:1: and the mixture was heated to 40°C -80°C and stirred.
10 Water (3.0 ml) was added to the stirred mixture to fully dissolve the cobalt and uranium nitrates. After stirring for 3 hours at 50°C, the mixture became a homogeneous solution. Then 8 grams of dried γ-alumina (particle size: 250 μm-300 μm) was added and the mixture was stirred to
15 allow the support to evenly contact the solution. The mixture was allowed to stand in air without stirring for 4 hours, and was then transferred to a quartz boat and combusted at 500°C for 10 minutes. The product was formed as black particles and was used as a precursor for a Fischer-
20 Tropsch catalyst system.

Example 2

Preparation of a cobalt and zirconia Fischer-Tropsch
synthesis catalyst

25 Co(NO₃)₂.6H₂O (17.7 g) was mixed with ZrO(NO₃)₂.2H₂O, (1.32g), urea (15.6 g) was added in a ratio of urea to metal of 4:1, and the resulting mixture was heated to 60°C and stirred. Water (2.0ml) was added to the mixture while stirring. The
30 cobalt nitrate and zirconium nitrate dissolved completely after stirring for 3 hours at 60°C to form a homogeneous solution. The mixture was then transferred to a quartz boat and combusted at 500°C for 10 minutes. The product was formed as black particles and was used as a precursor for a Fischer-Tropsch catalyst system.

605 m²/g; particle size: 250 μm-350 μm) was added to the mixture. The mixture was stirred to allow the support to contact the solution. Afterwards, the mixture was allowed to stand in air at 50°C for 4 hours. It was then transferred to a quartz boat and combusted at 500°C for 10 minutes. The resulting black particles have a low density of 0.48 g/ml and were used as the catalyst precursor.

Elemental analysis on the catalyst precursor reveals that besides the Co, Si, Zr and O, the precursor also contains 0.1 wt% carbon. Further experiments show that the carbon content depends on the combustion temperature and atmosphere. Lower temperature combustion in static air leads to a higher carbon content in the precursor, while high temperature combustion in flowing air leads to precursors with lower carbon content or even no carbon deposition.

The catalyst precursor has Co present mainly as Co₃O₄. Co metal and/or oxycarbide and/or carbide may also be present. Three separate preparations of the catalyst gave a product with almost identical XRD patterns showing that the method was reproducible.

Example 3

Preparation of platinum catalyst for partial oxidation of methane

H₂PtCl₆ (0.4g) was mixed with urea (16.8 g), ammonium citrate (3.2 g) and water (25 ml). The mixture was heated to dissolve the platinum compound. Then KNO₃ (3.2 g) was added to the stirred solution to give a homogeneous solution.

Dried γ - Al_2O_3 (30 grams) was added and the mixture was blended for 2 hours at 40°C and heated gradually to remove the volatiles. The resulting solid material was transferred to a quartz boat and combusted in a Muffle oven at 600°C in air for 10 minutes. The resulting black particles were used as the catalyst precursor for alkane partial oxidation to synthesis gas.

Example 4

10 Preparation of a CoMo hydrotreating catalyst

Co(NO_3) $_2$.6H $_2$ O (0.9g) and (NH $_4$) $_6$ Mo $_7$ O $_{24}$.4H $_2$ O (1.8g) were blended with urea (4.5 g) and ammonium citrate (0.5 g). Water (6 ml) was added and the mixture was stirred at 40°C for 4 hours to give a homogeneous pink "jelly-like" material. Then
15 dried alumina (10.8 g) was added and the mixture was stirred for 2 hours. Heating was applied until the product becomes essentially dry. The mixture was transferred into an open quartz boat and combusted at 500°C for 10 minutes. The
20 resulting metal oxide material was used as a hydrotreating catalyst precursor.

Example 5

Preparation of zeolite X supported noble metal catalyst for hydrogenation of benzene

25

Zeolite X (2.2 g, ball-like support, 2-5mm in diameter) was first impregnated with 1.8ml of 2 M aqueous solution of ammonium citrate and the mixture was stirred for 2 hours and then dried at 250°C . The ammonium citrate was supported on
30 the zeolite X. The dried support was impregnated by
turning which

room temperature for 20 hours. The product was then dried at 120°C for 2 hours and combusted in a Muffle oven at 600°C for 10 minutes. It is seen that a black uniform layer is formed in the outer layer of the ball-like support, suggesting that the noble metal is distributed mainly on the external surface of the support. This is called an "egg-shell" catalyst (evidenced by TEM data).

Example 6

10 Preparation of a cobalt Fischer-Tropsch synthesis catalyst precursor

Calcined MCM-41 (180 μm -350 μm) (2.3 g) was impregnated with 3.2 ml of 2.0 M ammonium citrate and dried at 250°C for 2 hours. The resulting MCM-41/citrate material was then kneaded with $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.8 g) for 3 hours until the cobalt nitrate appeared to be evenly mixed with the MCM-materials. The kneaded mixture was transferred to a crucible and combusted at 400°C in air for 5 minutes to give the precursor of a MCM-41 supported cobalt catalyst for use in a Fischer-Tropsch synthesis.

Example 7

Preparation of a cerium zirconium catalyst material

25

$\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ ($0 < x \leq 1$) is one of the most important materials in the three-way motor catalyst system. This material is normally prepared by a precipitation method, by mechanical mixing the two metal compounds and then calcination, or by an emulsion method. The precipitation method can lead to uniform oxide composites, but the filtration and separation steps can present difficulties also there is waste water in

the preparation process. The mechanical method does not give a uniform phase of the oxide composites and some Ce or Zr oxide rich phases are also present. The emulsion method requires costly organometal-containing Ce or Zr compounds, which are used to give the uniform high surface area mixture.

In this Example, cerium nitrate was mixed with zirconium nitrate in the desired ratio, and then mixed with urea and ammonium citrate at a ratio of urea to metal sum of 3:1 and ammonium citrate to metal of 0.5:1. Water was added to the mixture at the mole ratio of water to metal of 1. The mixture was stirred vigorously and heated gradually to 60°C to give a yellowish transparent gel. The gel was transferred to a crucible and combusted at 700°C for 30 minutes. A uniform high surface area ($50.8\text{m}^2/\text{g}$) $\text{Ce}_x\text{Zr}_{(1-x)}\text{O}_2$ was thus obtained.

Example 8

Preparation of a nickel catalyst

$\text{Ba}(\text{NO}_3)_2$ (0.5g) was mixed with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, (19.64 g), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8g) and urea (6g). The mixture was heated to 50°C and blended until a transparent gel was obtained. In case there was still some undissolved material, a little water was added slowly while stirring until all material was dissolved. The resulting gel was transferred to an open crucible and combusted at 600°C in the air for 20 minutes. A Ba-modified alumina support supported nickel catalyst precursor was thus prepared.

Example 9

Preparation of catalyst precursor for CoW bimetal-containing
carbides

5 Co(NO₃)₂·6H₂O (3.6g) was mixed with (NH₄)₁₀W₁₂O₄₁·2H₂O (6.2g),
urea (8.6g), ammonium citrate (3.2g) and water (5 ml). The
mixture was heated to 65°C and stirred for 3 hours to form a
gel in which the ammonium tungstate was not completely
dissolved. This gel was then transferred to a quartz boat
10 and combusted at 500°C in the air for 1 hour. A CoWO_x with
surface area of 20 m²/g and uniform Co and W distribution was
thus obtained, as shown by Confocal Laser Raman and SEM
results.

Example 10

Fischer-Tropsch Synthesis

15 The catalyst precursor produced in Example 2 was reduced at
1°C/min to 400°C under flowing H₂ (GHSV: 3000h⁻¹), kept at
20 this temperature for 4 hours, cooled down to 180°C and then
used for a Fischer-Tropsch synthesis reaction. The reaction
conditions were: 30 bar, GHSV: 1500 h⁻¹, H₂/CO=2, catalyst
loading amount of 10 ml, 18 vol % N₂ was contained in the
feedstock. The reactor temperature was adjusted to control
25 the CO conversion.

The selectivity to CO₂ and CH₄ was found to be 0% and 6.2%
respectively, while the selectivity to C₅⁺ is more than 90%
under a CO conversion of 67%. The excellent performance of
30 this catalyst is thought to be due to distribution of Co
containing particles in a uniform manner and predominately

on the outer surface layer of the silica support, as indicated by SEM and TEM data.

When the catalyst was reduced at 1°C/min to 400°C under
5 flowing 20% CH₄/H₂ and kept for 4 hours, cooled to 210°C and
Fischer-Tropsch synthesis carried out at 8 bar, H₂/CO=2, GHSV
2000h⁻¹, CO conversion was found to be more than 85% and
selectivity to C₅⁺ more than 85%.

10

EXAMPLE 11

The procedure of Example 9 was repeated to prepare three
further CoW bimetal-containing carbides, which were compared
with a catalyst prepared by a method in which an organic
15 compound was not used. The catalysts were used for methane
partial oxidation to syngas. The catalyst preparation
details are seen in Table 1. XRD and SEM characterization
results show that Catalysts A and B have a more uniform Co
and W distribution than comparative catalyst D. After
20 carburisation, phase separation occurs in catalyst D,
although some phase separation was also in seen in catalyst
B..

TABLE 1

	Preparation details
Catalyst A	calcination of gel of $[(0.4)\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + (0.6)\text{WO}_3 + 2\text{Urea}]$ (mole ratio) at 650°C , then carburised with $20\%\text{CH}_4/\text{H}_2$ to 750°C for 2 hours
Catalyst B	calcination of $[(0.4)\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + (0.6)(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 2\text{H}_2\text{O} + 2\text{Urea}]$ (mole ratio) at 650°C , carburised with $20\%\text{CH}_4/\text{H}_2$ to 800°C for 2 hours
Catalyst C	Stir the gel of $(0.4)\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + (0.6)(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot 2\text{H}_2\text{O} + 2\text{Urea}$ (mole ratio) and Al_2O_3 at 60°C for 4 hours, calcined the system at 650°C to get $17\% \text{Co}_{0.4}\text{W}_{0.6}\text{O}_x / \text{Al}_2\text{O}_3$, then carburised with $20\%\text{CH}_4/\text{H}_2$ to 800°C for 2 hours
Catalyst D	Mixing $(0.4)\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + (0.6)\text{WO}_3$ and calcined at 700°C for hours, carburised then carburised with $20\%\text{CH}_4/\text{H}_2$ to 800°C for 2 hours

5 Catalyst D was formed by a mechanical mixture and calcination method following the procedure of CN-A-R79134.

The XRD patterns of catalysts A and B are almost the same, suggesting that the precursors of tungsten have little
 10 effect on the structure of the oxides, although the resultant carbides have substantial difference in the structure.

The structure of catalysts A and D were investigated using XRD. The bimetal-containing carbide in catalyst C is so highly dispersed over alumina that the XRD peaks of the carbide are not obvious. The structure of catalyst A is different from that of catalyst D. The main phase in catalyst A is WC, rather than W_2C , and the Co is highly dispersed in the carbide.

The activity of the catalyst A in the partial oxidation of methane (reactants composition: $2.4CH_4 + O_2$ (Air)) was measured under the following conditions: 5 bar, $830^\circ C$ and GHSV: $30,000h^{-1}$. Catalyst A shows higher methane conversion than catalyst B, but the selectivity to H_2 and CO for the two catalysts is almost the same. Catalyst A possesses higher activity and selectivity than catalyst D.

An activity test of catalyst C (Co and W content: 17wt%) for methane partial oxidation at 5 bar and $830^\circ C$ shows that methane conversion and H_2 & CO selectivity closely approach thermodynamic equilibrium values. The catalyst is stable for at least in 7 days, and no carbon deposition is seen in the catalyst bed. This is probably because the presence of tungsten depresses the carbon deposition.

25

Example 12

The process of Example 4 was repeated to prepare catalysts containing different amounts of Mo and Co, and these catalysts were used in a thiophene hydrodesulfurisation (HDS) process. The results are shown in Table 2.

30

Table 2

Catalyst	Mo loading wt%	Co loading wt%	Precursor Preparation Method	Pre- treatment	Thiophene Conv, %	HDS rate, mmol/s.g
4-1	9.43	2.17	OMXC	Sulfurization	78.4	0.33
4-2	11.47	2.09	OMXC	Sulfurization	80.1	0.34
4-3	7.27	2.24	OMXC	Sulfurization	60.1	0.25
4-4	9.48	1.63	OMXC	Sulfurization	62.9	0.26

5

The amount of Mo and Co was found to have a significant effect on the catalyst performance for thiophene HDS. A decrease in the Mo content and an increase Co content does not improve the catalyst performance. This may be because
 10 Mo is the active component, and the Co serves as a promoter for the reaction.

The XRD patterns of catalysts 4-1, 4-2, 4-3 and 4-4 show no peaks due to Co or Mo oxides. This indicates that the Co
 15 and Mo oxides are highly dispersed in the alumina support.

Example 13

The activity of Catalyst 4-3 as defined in Example 12 in a
 20 thiophene HDS process was compared with that of a catalyst prepared by an impregnation method. The results are shown in Table 3.

Table 3

Catalyst	React. Temp, °C	Pretreatment	Thiophene Conv, %	HDS rate, mmol/s.g
4-3	350	Sulfurization	79.1	0.33
4-3	380	Sulfurization	79.3	0.33
4-3	350	Carburization	28.7	0.12
4-3	380	Carburization	34.0	0.14
3-3-im	350	Sulfurization	15.8	0.07
3-3-im	380	Sulfurization	24.3	0.10
3-3-im	350	Carburization	12.0	0.05
3-3-im	380	Carburization	20.4	0.09

5 Catalyst 4-3 has a higher activity than that of catalyst 3-3 in both the sulfide and carbide form. However, the sulfide catalysts have much higher performance for thiophene conversation than the carbide catalysts.

10 Catalyst 3-3-im was also characterized with XRD. The catalysts 4-1, 4-2, 4-3 and 4-4 have only the diffraction peaks of the support and Al metal, which is the sample holder, and no Mo oxide diffraction peaks are observed. However, in Catalyst 3-3-im, small peaks due to the

11 diffraction of MoO₃ can be observed in the

impregnation method does not disperse the MoO_3 well over the alumina support.

The Raman spectra of Co-Mo-O/ Al_2O_3 catalysts 4-1 and 3-3-im
5 were measured. The intensity of CoMoO_4 peak is weaker in catalyst 4-1 than in Catalyst 3-3-im, although the content of Co and Mo are equivalent, indicating that Catalyst 4-1 has higher and more uniform Co and Mo dispersion, which may be the reason for the improved performance in HDS.

CLAIMS

1. A process for preparing a supported catalyst or catalyst precursor comprising:
 - 5 a. preparing a liquid mixture of (i) a catalyst support or a catalyst support precursor; (ii) a metal-containing compound and (iii) a polar organic compound which acts as a solvent for the metal-containing compound;
 - b. converting said mixture to a paste or solid
10 residue; and
 - c. combusting the residue in an oxygen-containing atmosphere to at least partially convert the organic compound to carbon and to form said supported catalyst or catalyst precursor.
15
2. A process according to claim 1 wherein the polar organic compound is liquid at 20°C.
3. A process according to claim 1 wherein the polar
20 organic compound is solid at 20°C and the liquid mixture is formed by melting the polar organic compound.
4. A process according to any one of the preceding claims in which the liquid mixture comprises a solid catalyst
25 support and the metal-containing compound dissolved in the polar organic compound.
5. A process according to any one of claims 1 to 3 wherein the catalyst support precursor is dissolved in said liquid
30 mixture and forms the support during the heating and/or the combustion step.

6. A process according to any one of the preceding claims wherein the liquid mixture further comprises water.

7. A process for preparing a supported catalyst or
5 catalyst precursor comprising:

a. preparing a mixture of (i) a porous catalyst support and (ii) an organic compound in a solvent;

b. removing the solvent such that the polar organic compound is deposited in the pores of the catalyst support;

10 c. mixing the catalyst support with a solution of a metal-containing compound and removing the solvent to form a solid residue or kneading or mechanical mixing the catalyst support with a metal-containing compound; and

d. combusting the resultant solid in an oxygen-
15 containing atmosphere to at least partially convert the organic compound to carbon and to form said supported catalyst or catalyst precursor.

8. A process according to any one of the preceding claims
20 wherein the metal-containing compound comprises a transition metal of the f-block or d-block of the periodic table.

9. A process according to any one of the preceding claims wherein the polar organic compound is an organic amine,
25 amide, urea, an organic carboxylic acid, an alcohol, an amino acid, a heteroaromatic compound or a surfactant.

10. A process according to claim 9 wherein the polar organic compound is urea, a citrate or citric acid.

11. A process according to any one of the preceding claims wherein the final catalyst or catalyst precursor support is an oxide, carbide, oxycarbide, zeolite, or boronnitride.

5 12. A process according to any one of the preceding claims where the combustion is carried out for 15 minutes or less.

13. A process according to any one of the preceding claims wherein the combustion is carried out in air.

10

14. A process according to any one of the preceding claims where the combustion is carried out at a temperature of from 150 to 1000°C.

15 15. A process according to any one of the preceding claims where the catalyst or catalyst precursor before activation comprises carbon in an amount of up to 8 wt% based on the total weight of the catalyst or catalyst precursor.

20 16. A process according to any one of the preceding claims wherein the catalyst or catalyst precursor is a Fischer-Tropsch synthesis, hydrotreating or hydrocarbon partial oxidation catalyst or catalyst precursor.

25 17. A process for carrying out a Fischer-Tropsch synthesis, hydrotreating or hydrocarbon partial oxidation reaction, which comprises catalysing said reaction with a catalyst prepared by a process as defined in claim 15.

30 18. A Fischer-Tropsch synthesis catalyst or catalyst precursor comprising, on an inert support.

ii) 1 to 10wt% promoter selected from zirconium, uranium, titanium, thorium, hafnium, cerium, lanthanum, yttrium, magnesium, calcium, strontium, cesium, rubidium, molybdenum, tungsten, chromium, manganese, rhenium and rare
5 earth elements; and

iii) carbon in an amount of up to 8 wt%;
the above percentages being based on the total weight of the supported catalyst.

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